From this standpoint one might reasonably expect to find non-specific anionic inhibitors for these enzymes even though they are not metal-activated.

One is inclined also to wonder whether cationic detergent molecules would not catalyze reactions such as peptide hydrolyses in basic solution by a mechanism similar to those outlined above. It may be necessary to use a detergent of the type R—NH$_3^+$ rather than R—N(R')$_3^+$ in order to take advantage of hydrogen-bond formation in the stabilization of the intermediate complex. Substrates with a net negative charge and detergent concentrations above the critical micelle value should be particularly favorable.

It seems, therefore, that the behavior of metals as activators of hydrolyzing enzymes can be understood within the framework of the mechanisms established for simpler systems.[33,34] Little is gained and much that is perplexing is introduced by added assumptions of chelate formation. It does not follow, of course, that chelate formation is not an essential prerequisite in other metal-activated enzyme systems. A convincing case can only be established, however, if the postulated properties do not conflict with the known behavior of metals as chelating species and as mediators in the binding of small molecules to proteins.

EVANSTON, ILLINOIS

The Infrared Spectra of Nitroguanidine and Related Compounds

BY W. D. KUMLER

The infrared spectra of nitroguanidine and six related compounds were obtained on mulls in perfluorokerosene. Six of the compounds have two or more bands in the 3 μ region giving evidence of considerable hydrogen bonding. 1-Nitro-2-nitrimino-imidazolidine has one narrow band at 3.02 μ which according to the current practice could be ascribed to a free N–H vibration. However, it appears probable that it may also arise from a hydrogen bonded N–H. The presence of a broad band in the 3 μ region for azo-bis-(chloroformamidine) indicates N–H $\cdots$ N bonds of appreciable strength. All the compounds have bands at 5.92–6.18 μ attributed to C=N and those containing nitro groups have bands at 6.11–6.38 μ attributed to NO$_2$. The frequency of the nitro bands changes in the same way as the C=N bands giving evidence that the two are conjugated. The shift in frequency is correlated with the contribution of resonating forms with a separation of charge. This behavior is further evidence that these compounds are nitrimines.

The infrared spectra of nitroguanidines and related compounds are of interest because they contain hydrogen bonds of the type N–H$\cdots$O and N–H $\cdots$N and because recent work[1-5] based on chemical dipole moment and dissociation constant data has shown that a number of guanidine derivatives have structures different from those commonly assigned to them. Nitroguanidine, for example, is a nitro-imine (nitrimine) H$_2$N—C(=NH$_2$)=N—NO$_2$ and not a nitro-amine (nitramine) H$_2$N—C(=NH)—N—NO$_2$, as it is usually written. The infrared spectra are in agreement with the recent extensive evidence that these compounds are nitrimines.

The only prior measurements of the infrared spectra of compounds of this type were carried out by Lieber, Levering and Patterson.[6] Their compounds were measured as mulls in white mineral oil and unfortunately this solvent itself has high absorption between 3 and 4 μ and 6 and 7 μ. This interferes with the measurement of the true absorption characteristics of the compounds themselves around 3 and 6 μ where the N–H stretching and double bond stretching frequencies occur. In interpreting their results they have assumed that the >C=NH group is present in all guanidine derivatives which recent evidence has shown is not the case.

The compounds in this work were all measured from 1 to 15 μ as mulls in perfluorokerosene, a solvent that is relatively free of absorption in the most interesting regions around 3 and 6 μ. A Perkin–Elmer Model 21 Infrared Spectrograph with a sodium chloride prism was used. The nitroguanidine and nitroaminoguanidine were those used in previous measurements.[3] The others were supplied to us by Professor George F Wright. These compounds gave no evidence of decomposition. The melting points of those compounds in which this property is an indication of purity were unchanged at the time of measurement from those originally reported.

All the compounds measured except 1-nitro-2-nitriminoimidazolidine have two or more bands in the 3 μ region, giving considerable absorption over a range of 300 or more cm.$^{-1}$. Four of the compounds, 2-nitroiminoimidazolidine, nitrosoguanidine, azo-bis-(chloroformamidine) and azo-bis-(nitroformamidine) have two bands around 3 μ, a narrow band in the 2.97–3.03 μ region and a broader band in the 3.21–3.30 μ region. In the

(1) S. S. Barton, R. H. Hall and G. F Wright, THIS JOURNAL, **73**, 2201 (1951).

(2) W. D. Kumler and P. P. T. Sah, J. Am. Pharm. Assoc. Sci. Ed., **41**, 373 (1952).

(3) W. D. Kumler and P. P. T. Sah, J. Org. Chem., **18**, 669 (1953).

(4) W. D. Kumler, ibid., **18**, 676 (1953).

(5) W. D. Kumler, THIS JOURNAL, **75**, 3092 (1953).

(6) E. Lieber, D. R. Levering and L. J. Patterson, Anal. Chem., **23**, 1594 (1951).

case of 2-nitroiminoimidazolidine and azo-bis-(chloroformamidine), there are shoulders on the broad band which give an indication of a third band. Nitroaminoguanidine has three distinct bands and nitroguanidine four bands in the 3 μ region. From the evidence which has accumulated indicating that when an OH or NH group is involved in hydrogen bonding that the characteristic stretching band will be shifted to lower wave lengths and broadened,[7] it can be inferred that all these compounds showing one or more broad bands in the 3.0 to 3.3 μ region have hydrogen bonds in their crystals.

The possibility that some of these bands are the first harmonics of the bands around 6 μ is not likely for the extinctions of the bands at 3 μ are much too high compared with those at 6 μ to be harmonics of the latter. The symmetrical and antisymmetrical vibrations of NH_2 groups would give rise to two bands. Such bands are usually separated by 100 cm.$^{-1}$ or less, but some of these bands are considerably farther apart. There are a number of ways that the amino groups could be hydrogen bonded which would give rise to different wave length bands. The situation is somewhat analogous to that for the simple alcohols where three wave lengths for different types of hydrogen bonding have been identified.[8] More possibilities exist in the case of these nitrogen compounds since intra- as well as intermolecular hydrogen bonds can be present and the hydrogens can bond to two or more types of nitrogen atoms as well as to oxygen atoms. Thus there are more theoretical bands possible arising from the hydrogen bonded N–H than have been observed under our conditions of measurement. It is to be noted that our curves show more bands in this region than have been reported by previous workers.[6]

The one narrow band at 3.02 μ in case of 1-nitro-2-nitroiminoimidazolidine could possibly arise from a free N–H group. The structure of the compound, however, makes such a possibility unlikely as there is an excellent opportunity for the compound to have an intramolecular hydrogen bond.
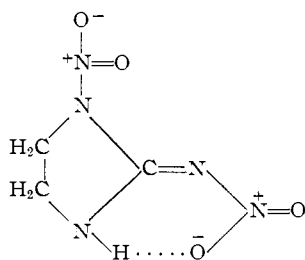
If for some unknown reason such a configuration is excluded, there appears to be no reason why this hydrogen should not form an intermolecular hydrogen bond with a neighboring molecule.

The fact that only one narrow band is found in this region indicates that we are not dealing with a situation where some of the molecules have free, others intra, and still others intermolecular hy-

(7) F. A. Miller in "Organic Chemistry," Vol. III, edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 153.

(8) F. A. Smith and E. C. Creitz, J. Research Natl. Bur. Standards, 46 [2], 145 (1951).

drogen bonds, for in that case there would be more and broader bands. Clearly, there appears to be only one type of N–H group and the most likely one is an intramolecular hydrogen bonded N–H group. For a hydrogen bonded N–H to have one narrow band of this type, while unusual, is not without precedence for another compound known to contain a very strong N–H⋯O bond and having a very narrow band at 3.03 μ has been reported.[9] The shortest wave length bands in the other compounds may also arise from hydrogen bonded N–H groups. All compounds have a larger number of lone electron pairs on oxygen and nitrogen than they have hydrogen atoms attached to nitrogen so there are more than enough lone electron pairs to hydrogen bond all available hydrogen atoms. Whether they actually are all bonded would depend in part on steric considerations. The position of the bands in the 3 μ region suggests that the hydrogens may be all bonded.

The compounds all have bands in the 6 μ region and these could arise from C=N stretching, N=O stretching in nitro or nitroso groups and N–H

TABLE I[a]

	Microns	Probable assignments
H₂C—HN⟩ C=N—NO₂ H₂C—HN⟩ 2-Nitriminoimidazolidine	2.97 3.25 6.18 6.38	N–H N–H C=N Nitro
H₂C—N—NO₂ ⟩ C=N—NO₂ H₂C—NH 1-Nitro-2-nitriminoimidazolidine	3.02 6.09 6.15 6.37	N–H C=N Nitro Nitro or N–H bend
H₂N⟩ C=N—NO₂ H₂N⟩ Nitroguanidine	2.96 3.01 3.13 3.20 6.01 6.11	N–H N–H N–H N–H C=N Nitro
H₂N—HN⟩ C=N—NO₂ H₂N⟩ Nitroaminoguanidine	2.99 3.08 3.17 5.98 6.16 6.32	N–H N–H N–H C=N Nitro N–H bend
H₂N⟩ C=N—NO H₂N⟩ Nitrosoguanidine	3.03 3.30 5.92 6.08 6.65	N–H N–H C=N N–H bend Nitroso
Azo-bis-(chloroformamidine)	2.98 3.21 6.04 6.41	N–H N–H C=N N–H bend
Azo-bis-(nitroformamidine)	3.02 3.23 6.07 6.38	N–H N–H C=N Nitro or N–H bend

(9) Professor R. M. Badger, private communication.

bending vibrations. The double bond stretching vibrations would be expected to give rise to the most intense bands. The bands resulting from N–H bending may be obscured in some cases by the double bond stretching bands since there is a common region around 6 μ where these bands may overlap.

The C=N stretching bands usually occur at shorter wave lengths than the nitro bands.[10] The probable assignments of the various bands in the 3 and 6 μ regions are given in Table I. If these compounds are nitrimines as recent work indicates,[1–5] then the C=N bond is conjugated with the nitro group and any contribution from forms with a separation of charge such as

$$\underset{H_2N}{\overset{\overset{+}{H_2N}}{\diagdown}}C-N=\overset{+}{N}\underset{\diagdown O^-}{\diagup^{O^-}}$$
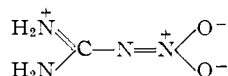
will reduce the amount of double bond character in the imine double bond and also the amount of double bond character in the nitro group. The frequency of the corresponding bands will be lowered by such changes. One would then expect the frequency of the band corresponding to the nitro group to change in the same way as the one corresponding to the imine C=N group, and that these changes would be related to the relative contribution of the resonating forms with a separation of charge. The compound expected to have the greatest contribution of these forms is 2-nitro-iminoimidazolidine since it has forms of equal energy and has a carbon and hydrogen attached to the nitrogens that assume the plus charge, instead of two hydrogen atoms. The C=N and nitro group in this compound should have the most single bond and the least double bond character and therefore the lowest frequencies. Such is the case with values of 1618 and 1567 cm.[-1] for these two bands.

(10) Reference 7, pp. 140–141.

1-Nitro-2-nitriminoimidazolidine would have less contribution from these forms since it has essentially only one form with a separation of charge and the frequencies here are 1642 and 1626 cm.[-1].

Nitroguanidine has forms of equal energy, but the H_2N-groups accept less readily the plus charge than a C–NH– group. Apparently the latter is the more important factor for the frequencies in this compound are 1664 and 1637 cm.[-1], indicating more double bond character in the C=N and the nitro group than in the previous compound.

Nitroaminoguanidine would be expected to have a smaller contribution from the forms with a separation of charge than nitroguanidine because the forms are no longer equivalent. Such is the case for the C=N band has a frequency of 1672 cm.[-1], but the nitro band in this case is anomalous being at 1623 cm.[-1]. This may result from the large amount of hydrogen bonding reducing the frequency of the nitro group.

Nitrosoguanidine would be expected to have the least contribution from the forms with a separation of charge and its C=N group has the highest frequency 1689 cm.[-1] as anticipated. The nitroso frequency of 1504 cm.[-1] is higher than the usual unconjugated nitroso range.[10] But since conjugation causes the nitro group to absorb at higher frequencies,[10] the same behavior is likely for the nitroso group. The higher absorption frequency for the nitroso group thus indicates that the nitrimine structure for this compound is correct. The behavior of the bands around 6 μ in all these compounds supports the other extensive evidence that the compounds are nitrimines.

I wish to express my appreciation to Professor Richard M. Badger for his expert advice and counsel during the entire course of this investigation, and to Professor George F. Wright for supplying five of the compounds.

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Lead Salts of 2,4,6-Trinitroresorcinol

BY RALPH A. ZINGARO

A method for the preparation of pure normal and basic lead styphnate is described, and two new salts, including dipyridin-lead(II) styphnate, have been prepared. A study of some of the physical properties of these salts and a consideration of the chemistry involved in their preparation raises a question as to the structure of these salts. Structures for these compounds, based on the observations reported, are discussed. The infrared spectra of normal and basic lead styphnate and of styphnic acid have been measured, and observations relating to them are reported.

Although lead salts of styphnic acid (2,4,6-trinitroresorcinol) have been known for many years and have found extensive military and commercial use as electrical initiators for explosive charges, little effort has been devoted to a better understanding of their chemical nature. The information relating to them is confined very largely to the patent literature and is concerned almost wholly with commercial preparation methods.

Griess[1] reported a basic salt of lead styphnate to which he assigned the formula $C_6H(NO_2)_3O_2Pb$·

(1) P. Griess, Ber., **7**, 1224 (1874).

$PbO·1^1/_2H_2O$, and Herz[2] claimed the first preparation of anhydrous, normal lead styphnate. There are a variety of patented procedures for the preparation of a normal salt hydrate and a basic salt for which structures I and II[3] have been generally accepted. The preparation of these salts, as usually described, involves the direct combination of solutions of a soluble lead salt and an alkali (or alkaline earth) metal styphnate. The conditions of pH,

(2) E. Herz, U. S. Patent 1,443,328 (1919).

(3) J. Taylor, "Detonation in Condensed Explosives," Oxford University Press, New York, N. Y., 1952, p. 13.